PB86-136538

# EPA (Environmental Protection Agency) Method Study 32: Method 450.1 Total Organic Halides (TOX)

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Prepared for

Environmental Monitoring and Support Lab.-Cincinnati, OH

Dec 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-136538

EPA/600/4-85/080
December 1985

# EPA METHOD STUDY 32

# METHOD 450.1 - TOTAL ORGANIC HALIDES (TOX)

by

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SPRINGFIELD, VA. 22161

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| | | |
|---|---|---|
| 1. REPORT NO. EPA/600/4-85/080 | 2. | 3. RECIPIENT'S ACCESSION NO. PB86 136538/AS |
| 4. TITLE AND SUBTITLE<br>EPA Method Study 32:<br>Method 450.1 - Total Organic Halides (TOX) | | 5. REPORT DATE<br>December 1985<br>6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>Tate, C. H.; Clark, R. R.; Chow, B. M.; Grams, N. E.; and Hashimoto, L. K. | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>James M. Montgomery Consulting Engineers, Inc.<br>555 East Walnut Street<br>Pasadena, CA 91109-7009 | | 10. PROGRAM ELEMENT NO.<br>5CBL6<br>11. CONTRACT/GRANT NO.<br>68-03-3163 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Monitoring and Support Laboratory<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Cincinnati, OH 45268 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>14. SPONSORING AGENCY CODE<br>EPA 600/6 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report describes the interlaboratory method study that was performed to evaluate interim Method 450.1 for total organic halides (TOX). In the method, a measured volume of water is passed through two columns in series, each containing 40 mg of activated charcoal. Organic halides (OX) present in the water are adsorbed on to the charcoal which is washed to eliminate trapped inorganic halides. The contents of the columns are then pyrolzed converting the halides to titratable species that are measured microcoulometrically. In this study, three water matrices, reagent water, ground water, and surface water, were spiked at six concentrations with a solution containing a combination of four model compounds. These were lindane, bromoform, pentachlorophenol, and tetrachloroethene. A chlorinated drinking water diluted to four concentrations with distilled water were also analyzed.

Ten laboratories participated in the study. Data obtained were analyzed using a standardized package known as Interlaboratory Method Validation Study (IMVS), which is designed to implement the recommendations of ASTM Standard D-2777. The IMVS package includes rejection of outliers; estimation of mean recovery as a measure of bias; estimation of single-analyst and overall precision, and tests for effects of water type on these parameters.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>Distribute to Public | 19. SECURITY CLASS (This Report)<br>Unclassified | 21. NO. OF PAGES<br>79 |
| | 20. SECURITY CLASS (This page)<br>Unclassified | 22. PRICE<br>$11.95 |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

## DISCLAIMER

The information in this document has been funded wholly by the United States Environmental Protection Agency under Contract Number 68-03-3163. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as a USEPA document.

## FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microorganisms in water and determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

This publication reports the results of a study of the carbon adsorption microcoulometric titration method for determining the concentration of organically bound halides in water. Federal agencies, states, municipalities, universities, private laboratories, and industry should find this evaluative study of vital importance in their efforts in monitoring and controlling halogenated organic pollution in the environment.

Robert L. Booth
Director, EMSL - Cincinnati

## ABSTRACT

This report describes the interlaboratory method study that was performed to evaluate Interim Method 450.1 for total organic halides (TOX). In the method, a measured volume of water is passed through two columns in series, each containing 40 mg of activated charcoal. Organic halides (OX) present in the water are adsorbed onto the charcoal which is washed to eliminate trapped inorganic halides. The contents of the columns are then pyrolyzed converting the halides to titratable species that are measured microcoulometrically. In this study, three water matrices; reagent water, groundwater, and surface water, were spiked at six concentrations with a solution containing a combination of four model compounds; lindane, bromoform, pentachlorophenol, and tetrachloroethene. A chlorinated drinking water diluted to four concentrations with distilled water were also analyzed.

Ten laboratories participated in the study. Data obtained were analyzed using EPA's computerized statistical program known as Interlaboratory Method Validation Study (IMVS), which is designed to implement the recommendations of ASTM Standard D-2777-77. The IMVS package includes rejection of outliers; estimation of mean recovery as a measure of bias; estimation of single-analyst and overall precision; and tests for effects of water type on three parameters.

This report was submitted in fulfillment of Contract No. 68-03-3163 by James M. Montgomery, Consulting Engineers, Inc. It covers work performed from September 1982 to June 1985.

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## ACKNOWLEDGEMENTS

The authors wish to thank the following persons for their help with the project: Albert R. Trussell, Eric Crofts, John Wanek, Shine Pearson, and Harry Morrow.

## SECTION 1

## INTRODUCTION

This project determined, by interlaboratory method study, the precision and bias of EPA Method 450.1 for total organic halide (TOX), a surrogate parameter used to measure the amount of halogen-containing organic material in a water sample. The method detects organically bound bromine, chlorine, and iodine but is not sensitive to organic fluorine compounds; nor does it provide structural information for any of the compounds comprising the TOX.

The halogenated organics measured by TOX are usually indicative of anthropogenic contamination. Compounds which contribute to TOX include organic cleaning solvents such as trichloroethene and 1,1,1-trichloroethane; chlorination products such as trihalomethanes (THMs), chlorophenols, certain pesticides and herbicides. In addition, TOX includes high molecular weight chlorinated compounds which generally comprise a higher percentage of organic halides (OX) than do THMs in chlorinated finished drinking water.

## SECTION 2

## CONCLUSIONS

The object of the study was to characterize the performance of Method 450.1 in terms of precision, bias, and the effect of water types on precision and bias. The regression equations shown in Table 1 are the result of statistical analyses of 220 analytical values. Twelve points were rejected as laboratory outliers, 10 were rejected by Cochran's test and seven as individual outliers. Rejected data totaled 12.2 percent of the 220 analytical values.

The bias of the method was estimated by comparing mean recoveries to true TOX values at six concentration levels between 38.7 and 441.1 μg/L. The average recovery calculated from the regression equations was 86.5 percent, with the actual recoveries ranging from 83.5 percent to 117.2 percent. The highest recoveries occurred at the lowest concentration levels.

The overall standard deviation, S, was not significantly dependent on recovery, $\bar{X}$, as indicated by slopes of regression equations which ranged from -0.0128 to 0.0374. The intercepts ranged from 6.4 to 14.1 and closely approximated the actual S values obtained for the low, medium and high concentration ranges: 2.9 to 14.4 μg/L, 5.7 to 14.1 μg/L and 10.4 to 15.4 μg/L, respectively. Percent relative standard deviations for low, medium and high Youden pair samples were 7.2 to 31.8 percent, 3.2 to 6.6 percent, and 3.0 to 4.4 percent, respectively.

The single-analyst precision $S_r$, indicating the precision associated with a single laboratory also showed little dependence on recovery, $\bar{X}$. The slopes of the regressions for $S_r$ ranged from -0.0092 to 0.0033 with intercepts ranging

TABLE 1. REGRESSION EQUATIONS FOR PRECISION AND BIAS

| Water Type | $\bar{X}$ | S | $S_r$ |
|---|---|---|---|
| Reagent | $\bar{X} = 0.807C + 14.1$ | $S = -0.0128\ \bar{X} + 14.2$ | $S_r = -0.0092\ \bar{X} + 12.7$ |
| Surface | $\bar{X} = 0.894C + 7.14$ | $S = 0.0374\ \bar{X} + 2.68$ | $S_r = -0.0109\ \bar{X} + 6.14$ |
| Ground | $\bar{X} = 0.896C + 6.38$ | $S = 0.0280\ \bar{X} + 3.40$ | $S_r = 0.0033\ \bar{X} + 5.48$ |
| Chlorinated Drinking Water | -- | $S = 0.0946\ \bar{X} - 9.22$ | $S_r = 0.1037\ \bar{X} - 0.1014$ |

---

$\bar{X}$ = Mean recovery (bias) as !g/L
S = Overall precision as !g/L
$S_r$ = Single-analyst precision as !g/L
C = True value as !g/L

from 5.48 to 12.7. Single-analyst precision values actually obtained for low, middle and high concentrations ranged from 5.7 to 12.3 µg/L, 4.5 to 9.3 µg/L, and 9.4 to 12.0 µg/L, respectively. Single-analyst relative standard deviations for low, middle and upper concentrations were 11.8 to 23.7 percent, 2.2 to 3.9 percent and 2.5 to 3.4 percent, respectively.

No regression equation for TOX recovery from chlorinated drinking water was calculated due to the absence of a true concentration value for that sample type. Regressions calculated for overall S and $S_r$ against mean analyzed value, $\bar{X}$, yielded an equation for S with a strongly negative intercept. The equation generated did not accurately predict the S values obtained from the study data and was considered invalid. The most probable cause for this was considered to be the use of four rather than six concentration levels for calculation of the regression. Individual S values for the four water samples ranged from 3.1 to 7.9 µg/L as for TOX concentrations between 63.8 µg/L and 83.6 µg/L. For TOX concentrations in the range of 137.8 to 178.5 µg/L, S values ranged from 12.7 to 29.6 µg/L. Single-analyst precision ranged from 4.5 at the low concentration range to 22.8 µg/L for the higher concentration range.

Statistical comparisons of the effect of water type were performed. No significant effect of water type on bias or precision of Method 450.1 was observed.

## SECTION 3

## RECOMMENDATIONS

Method 450.1 is recommended for the analysis of Total Organic Halide (TOX) in drinking, ground, and surface waters. The method bias and precision are acceptable and there are no significant matrix effects with the waters listed above. The "Interim" designation should be removed from the current title of the method.

- To ensure more consistent overall performance of the method, several ambiguous points that became apparent during Phase I of the study, should be clarified in future versions of the method.

- Additional research should be conducted on performance of the method when analyzing chlorinated drinking water supplies.

- In order to avoid TOX carry over from one sample to the next, the sample reservoir should be rinsed with two 100 ml volumes of reagent water before adding another sample.

- Users of this method must take precautions to avoid contamination of samples and the analytical system, especially when analyzing samples expected to have low TOX concentrations. The potential for contamination from contact with the fingers can be greatly reduced by following the recommendations found in Section 5.4.2 of the method.

## SECTION 4

## DESCRIPTION OF THE STUDY

### TEST DESIGN

The overall experimental design was governed by Youden's original non-replicate design for collaborative evaluation of precision and bias for analytical methods (1). The design is recommended by ASTM in Standard Practice D2777-77 "Determination of Precision and Bias of Methods of Committee D-19 on Water" (2). According to Youden's plan, paired samples containing analytes at similar but distinct concentrations are analyzed collaboratively by a group of laboratories. In this study, sample pairs were prepared at low, medium, and high TOX concentrations within the analytical range of the method. Samples were prepared as full volume aqueous solutions for shipment to 10 laboratories. No sample preparation was required of the analysts at the participating laboratories.

A summary of the test design according to Youden's design is given below:

1. Three Youden pairs were used for the analyses in reagent, ground and surface waters. A chlorinated drinking water was diluted to four concentrations constituting two Youden pairs.

2. The three Youden pairs were spread across the working range of the method.

3. Analyses for TOX were performed by 10 laboratories according to Method 450.1.

4. Each sample was analyzed in duplicate as required by the method. The means of duplicate results were analyzed statistically using the IMVS statistical package.

## Selection of Laboratories

The initial contacts with laboratories were made using an instrument placement list obtained from the manufacturer. Willing laboratories with equipment to perform TOX analyses according to Method 450.1 were asked to submit bids. Performance evaluation samples were sent to 16 laboratories including two EPA laboratories. Each of the 16 laboratories was evaluated on accuracy, ability to strictly adhere to the method, timeliness, and ability to follow reporting procedures. Based on these criteria, the eight paid and two unpaid EPA laboratories listed below were selected for participation.

Aquatec Environmental Services
75 Green Mountain Drive
South Burlington, Vermont 05401

Gascoyne Laboratories
27 South Gay Street
Baltimore, Maryland 21202

Harmon Engineering & Testing
1550 Pumphrey Avenue
Auburn, Alabama 36830

McKesson Environmental Services
6363 Clark Avenue
Dublin, California 94568

MMTL Analytical Services
206 South Keene Street
Columbia, Missouri 65201

Radian Corporation
8501 MoPac Boulevard
Austin, Texas 78766-0948

Spectrix Corporation
3911 Fondren, Suite 100
Houston, Texas 77063-5821

Timber Products
884 Blacklawn Road
Conyers, Georgia 30207

U.S. EPA
Office of Drinking Water
Technical Support Division
26 W. St. Clair Street
Cincinnati, Ohio 45268

U.S. EPA
Water Engineering Research
Laboratory
26 W. St. Clair Street
Cincinnati, Ohio 45268

**Phase I - Performance Evaluation**

Sixteen laboratories were provided with performance evaluation samples. The Phase I samples were prepared by spiking reagent water with sufficient lindane to give a TOX concentration of 220.9 µg/L as chloride. In order to present an analytical challenge, the sample also contained 25.6 µg/L of inorganic chloride as NaCl. Each laboratory received a single sample, a copy of Interim Method 450.1 (Appendix A), and a statement of conditions (Appendix B). Laboratories were required to submit the final results, blank values, standard and recovery results, raw data forms, and the signed statement of conditions within 10 days of sample receipt. The results were collected and evaluated for accuracy and completeness as described above. Laboratories with analytical problems were contacted to discuss and clarify analytical procedures.

**Phase II - Interlaboratory Method Study**

Water types used in this study were: (1) reagent water from the James M. Montgomery laboratory, (2) surface water from Azusa, (3) groundwater from Rubio Canyon (collected prior to chlorination), and (4) chlorinated drinking water from the Garvey Reservoir, operated by the Metropolitan Water District of Southern California. The waters were collected in clean five-gallon glass carboys. Nitric acid was added to the carboys prior to sampling as an inhibitor of possible biological degradation. The final pH of the water in each carboy was 1.0. Sodium sulfite was added to the distilled, ground and surface waters as a precaution against residual chlorine.

Triplicate subsamples were taken from each carboy of ground and surface water and analyzed for TOX background contamination. If TOX in excess of 5 µg/L was detected, the entire sample was heated, purged with nitrogen for 24 hours and cooled to room temperature. The procedure was repeated until re-analysis indicated no detectable TOX concentration.

The reagent, ground and surface waters were then spiked with a mixture of four halogenated organic compounds in methanol. Table 2 gives the composition of the spiking solution and the corresponding theoretical TOX concentration contributed by each component. The four compounds were chosen to represent differing properties including stability, volatility, polarity and type of halogenation. All four compounds are priority pollutants and indicators of industrial contamination. The water in each carboy was mixed by magnetic stirrer for one minute after addition of the spiking solution. Using a sampling tap, thirty-two 250 mL amber glass bottles were filled headspace-free. The TOX concentrations of the chlorinated drinking water were adjusted by dilution with reagent water. The target concentrations for these samples were near those of the low and medium Youden pairs of the spiked samples. The final TOX concentrations of the paired study samples are shown in Table 3.

Each bottle was labeled with a three letter code which identified the filling order, water type, and TOX concentration. Samples were stored in the dark at 4°C.

To establish verity, homogeneity and stability of the study samples, three bottles were randomly chosen from the beginning and end of the filling sequence and analyzed for TOX by Method 450.1. Verity was established if the mean result for each sample was 90 to 110 percent of the known TOX concentration. Table 4 indicates that all samples met the verity criterion. The samples were considered stable if "time zero" analyses were 90 to 110 percent of the later "time one" analyses. For this study, stability was established for periods of up to 140 days (Table 5).

Following verification of the study samples by two independent referee laboratories, packages were prepared for shipment to the participating laboratories. Sets of 18 spiked and four unspiked (chlorinated drinking water)

TABLE 2. THEORETICAL TOX CONCENTRATION OF SPIKING SOLUTION

| Compound | Concentration (μg/μL) | TOX (μg/μL as Cl) |
|---|---|---|
| Lindane | 2.736 | 2.001 |
| Pentachlorophenol | 3.026 | 2.014 |
| Bromoform | 4.184 | 1.761 |
| Tetrachloroethene | 2.294 | 1.962 |

TABLE 3. THEORETICAL TOX CONCENTRATIONS OF PAIRED STUDY SAMPLES

| Pair | Member | Concentration (µg/L) | Member | Concentration (µg/L) |
|---|---|---|---|---|
| Low Level | A1 | 38.69 | A2 | 54.17 |
| Mid Level | B1 | 193.4 | B2 | 243.7 |
| High Level | C1 | 386.9 | C2 | 441.1 |

TABLE 4. SUMMARY OF VERITY AND HOMOGENEITY DATA

| Sample ID | Youden Pair | Verity | | | Homogeneity |
|---|---|---|---|---|---|
| | | True Value µg/L as $Cl^-$ | Mean Analyzed Value µg/L as $Cl^-$ | Percent Recovery | Calculated F-Value |
| A | Chlorinated Drinking Water B-2 | N/A | 175.9 | N/A | 0.58 |
| B | Surface Water A-2 | 54.17 | 52.65 | 97.2 | 0.13 |
| C | Surface Water C-2 | 441.1 | 408.9 | 92.7 | 0.39 |
| D | Reagent Water B-1 | 193.4 | 176.0 | 91.0 | 3.1 |
| E | Chlorinated Drinking Water A-2 | N/A | 84.9 | N/A | 0.71 |
| F | Ground Water B-2 | 243.7 | 231.0 | 94.8 | 1.37 |
| G | Reagent Water C-2 | 441.1 | 396.8 | 90.0 | 0.13 |
| H | Surface Water C-1 | 386.9 | 360.5 | 93.2 | 0 |

TABLE 4 (Cont'd)

| Sample ID | Youden Pair | Verity: True Value µg/L as $Cl^-$ | Verity: Mean Analyzed Value µg/L as $Cl^-$ | Verity: Percent Recovery | Homogeneity: Calculated F-Value |
|---|---|---|---|---|---|
| I | Ground Water A-2 | 54.17 | 51.56 | 95.2 | 0.46 |
| J | Surface Water A-1 | 38.69 | 41.83 | 108.1 | 5.28 |
| K | Surface Water B-2 | 243.7 | 232.0 | 95.2 | 0.22 |
| L | Reagent Water A-2 | 54.17 | 51.35 | 94.8 | 0 |
| M | Chlorinated Drinking Water B-1 | N/A | 150.4 | N/A | 1.66 |
| N | Reagent Water C-1 | 386.9 | 352.7 | 91.2 | 2.05 |
| O | Chlorinated Drinking Water A-1 | N/A | 69.59 | N/A | 0.25 |
| P | Ground Water B-1 | 193.4 | 179.3 | 92.7 | 2.67 |
| Q | Reagent Water A-1 | 38.69 | 38.3 | 99.0 | 0.29 |

TABLE 4 (Cont'd)

| Sample ID | Youden Pair | Verity: True Value µg/L as $Cl^-$ | Verity: Mean Analyzed Value µg/L as $Cl^-$ | Verity: Percent Recovery | Homogeneity: Calculated F-Value |
|---|---|---|---|---|---|
| R | Ground Water C-1 | 386.9 | 359.6 | 92.9 | 14.08 |
| S | Ground Water A-1 | 38.69 | 41.2 | 106.5 | 0.54 |
| T | Surface Water B-1 | 193.4 | 177.0 | 91.5 | 0.07 |
| U | Reagent Water B-2 | 243.7 | 222.3 | 91.2 | 0.48 |
| V | Ground Water C-2 | 441.1 | 405.5 | 91.9 | 0.01 |

S = Significant difference at 0.01 level
N/A = Not applicable
NS = Difference is not significant at 0.01 level; degrees of freedom are (1,4) Critical F = 21.2

True Value = Theoretical TOX concentration
Mean Value = Measured TOX concentration

TABLE 5. STABILITY TEST SUMMARY

| | Sample Code | Time Zero Mean µg/L as $Cl^-$ | Time One Mean µg/L as $Cl^-$ |
|---|---|---|---|
| Distilled Water | | | |
| | Q | 33.12 | 30.95 |
| | L | 48.50 | 48.99 |
| | D | 195.83 | 181.15 |
| | U | 250.78 | 234.80 |
| | N | 381.84 | 360.96 |
| | G | 435.07 | 414.82 |
| Surface Water | | | |
| | J | 35.36 | 38.35 |
| | B | 49.64 | 52.27 |
| | T | 194.82 | 207.70 |
| | R | 252.10 | 239.24 |
| | H | 386.12 | 378.13 |
| | C | 441.63 | 430.54 |
| Groundwater | | | |
| | S | 33.17 | 34.04 |
| | I | 46.46 | 47.19 |
| | P | 197.40 | 197.60 |
| | F | 255.23 | 253.95 |
| | K | 394.73 | 379.38 |
| | V | 447.67 | 420.83 |
| Chlorinated Drinking Water | | | |
| | M | 117.68 | 110.88 |

samples were packed with refreezable gel packs into coolers. Each of the 10 shipments also contained a cover letter, chain-of-custody forms, TOX report forms, and a set of clarifications to Method 450.1. The pacakges were shipped early in the week by a major overnight courier. The laboratories were contacted to confirm delivery of intact samples.

## SECTION 5

## STATISTICAL TREATMENT OF DATA

This interlaboratory study was conducted to obtain information about the bias and precision associated with measurements by Interim Method 450.1 "Total Organic Halides". The statistical techniques employed in the data reduction process are similar to the techniques recommended in the ASTM Standard Practice D2777-77.

The algorithms required to perform the statistical analyses have been integrated by USEPA into a system of computer programs referred to as Interlaboratory Method Validation Study (IMVS) (3). The analyses performed by IMVS include:

- several tests for rejection of laboratory and individual outliers;
- summary statistics for mean recovery (accuracy), overall and single-analyst standard deviations;
- determination of the linear relationship between mean recovery and concentration level;
- determination of the linear relationship between the precision statistics and mean recovery, and
- testing for the effect of water type on bias and precision.

## REJECTION OF OUTLIERS

Outlying data points will occur in any set of data collected during an interlaboratory test program. It is important to identify and remove these data points because they can lead to summary statistics which are not representative of the general behavior of the method. However, some erratic behavior in the data may be directly related to some facet of the method under study. Therefore, seemingly unreliable data points should not be removed indiscriminantly, and any points that are removed should be clearly identified since further investigation of the analytical conditions related to the outliers might be of value. Data rejected as outliers for this study as a result of Cochran's test, Youden's laboratory ranking procedure, or the test for individual outliers have been identified by the symbol "*" in the raw data tables (Appendix C).

### Cochran's Test

Traditionally, only single determinations are required by analytical methods under study. Because, however, duplicate measurements are required by Method 450.1 and the IMVS software package does not allow entry of mean of duplicate values, it was necessary to calculate the mean of duplicate determinations. Prior to screening for outlying laboratories, an additional level of outlier testing was imposed in the form of Cochran's Test.

According to Cochran, if a standard deviation of one pair of duplicates is significantly different from the other standard deviations in that concentration group, then that pair belongs to a separate population and can be rejected subject to the significance level criteria below. The critiera for the rejection was 0.01 significance level for Cochran's "C" given by the formula shown below:

$$C = \frac{\text{largest } s_i^2}{\Sigma s_i^2}$$

$s_i$ = standard deviation of the ith pair of duplicates

Data rejected using Cochran's test are denoted by "CO" following the results in raw data tables (Appendix C).

**Youden's Laboratory Ranking Procedure**

Youden's (1) ranking test for outlying laboratories was applied separately to data from each water type used in this study. Each laboratory ranking test was performed at the five percent level of significance.

The Youden laboratory ranking procedure requires a complete set of data from every laboratory within a given water type. Missing data from laboratory i for sample type j were replaced by the following procedure. Letting $X_{ijk}$ denote the reported measurement from laboratory i for water type j and concentration level $C_k$, it is assumed that

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \varepsilon_{ijk}$$

where $\beta_j$ and $\gamma_j$ are fixed parameters which determine the effect of water type j, $L_i$ is the systematic error due to laboratory i and $\varepsilon$ is the random within laboratory error. Taking natural logarithms, it follows that

$$\ln X_{ijk} = \ln \beta_j + \gamma_j \ln C_k + \ln L_i + \ln \varepsilon_{ijk}$$

which is a linear regression model with dependent variable $\ln x_{ijk}$ and independent variable $\ln C_k$.

The natural logarithms of the individual laboratory's data were regressed against the natural logarithms of the true concentration levels for each water type. The predicted values $\ell n\ X_{ijk}$ were obtained from the regression equation, and any missing values for $X_{ijk}$ were estimated by $X_{ijk} = \exp(\ell n\ X_{ijk})$. (For complete details of this procedure see Reference 4).

If the ranking test rejected a laboratory for a specific water type, then all of the laboratory's data for that water type were rejected as outliers. The rejected values were excluded from all the remaining statistical analyses. In

values created to fill in the missing data were excluded from further statistical analyses.

**Tests for Individual Outliers**

The data remaining after the laboratory ranking procedure were grouped by water type. For each sample type, the data were divided into subsets defined by the concentration levels used in the study. Next, the test for individual outliers constructed by Thompson (5), and suggested in the ASTM Standard Practice D2777-77, was applied to the data using a five percent significance level. If an individual data point was rejected based on this test, it was removed from the subset, and the test was repeated using the remaining data in the subset. This process was continued until no additional data could be rejected.

## STATISTICAL SUMMARIES

Several summary statistics were calculated using the data retained after the outlier rejection tests were performed. These summary statistics include: the number of retained data points (n), the mean recovery ($\bar{X}$), bias as a percent relative error, the absolute overall standard deviation (S), the overall relative standard deviation (% RSD), the absolute single-analyst standard

deviation ($S_r$), and the single-analyst relative standard deviation (% RSD-SA). The formulas used to calculate these statistics are presented below where $X_1$, $X_2$. ..., $X_n$ denote the values of the n retained data points for each concentration level.

Mean recovery ($\bar{X}$):

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

Accuracy as a % Relative Error:

$$\%RE = \frac{\bar{X} - \text{True Value}}{\text{True Value}} \times 100$$

Overall Standard Deviation:

$$S = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (X_i - \bar{X})^2}$$

and

Percent Relative Overall Standard Deviation:

$$\%RSD = \frac{S}{\bar{X}} \times 100$$

The overall standard deviation, S, estimates the precision of measurements generated by a group of laboratories in the interlaboratory study. However, a measure of how well an individual analyst can expect to perform in his/her own laboratory is another important measure of precision. This single-analyst precision, denoted by $S_r$, was estimated for each Youden pair by

$$S_r = \sqrt{\frac{1}{2(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2}$$

where

$m$ = the number of complete Youden pair observations remaining after outliers have been removed,

$D_i$ = the difference between the observations in the Youden pair

and

$\bar{D}_i$ = average of the $D_i$ values

The single-analyst relative standard deviation was calculated by

$$\%RSD\text{-}SA = \frac{S_r}{\bar{X}^*} \times 100$$

where $\bar{X}^*$ is the average of the two mean recovery statistics corresponding to the two concentration levels defining the particular Youden pair.

These summary statistics provide detailed information on the bias and precision of the data obtained for each concentration level. One objective of the statistical analysis of the data is to summarize the information about bias and precision which is contained in the statistics.

Frequently a systematic relationship exists between the mean recovery ($\bar{X}$) and the true concentration level (C) of the analyte in the sample. In addition, there are often systematic relationships between the precision statistics (S and $S_r$) and the mean recovery ($\bar{X}$). Usually these systematic relationships can be adequately approximated by a linear relationship (i.e., by a straight line). Once these straight lines are established, they can be used to conveniently summarize the behavior of the method within a water type and can be used to obtain estimates of the bias and precision at any concentration level within the concentration range studied.

## STATEMENT OF METHOD BIAS

The bias of the method is characterized by the relationship of the mean recovery ($\bar{X}$) to the theoretical TOX concentration (C) in the water sample. In order to obtain a mathematical expression for this relationship, a regression line of the form

$$\bar{X} = a + b \cdot C \qquad (1)$$

was fitted to the data by regression techniques.

Often the true concentration values in a collaborative study cover a wide range. In such cases, the mean recovery statistics associated with the larger concentration values tend to dominate the fitted regression line producing relatively larger errors in the estimates of mean recovery at the lower concentration values. To reduce the overriding effects of high concentration, a weighted least-squares technique was used to fit the mean recovery data to the true concentration values. The weighted least-squares technique was performed by dividing both sides of Equation (1) by C resulting in Equation (2)

$$\frac{\bar{X}}{C} \cdot = a \cdot \frac{1}{C} + b \qquad (2)$$

The ($\bar{X}$/C) values were regressed against the (1/C) values using ordinary least squares to obtain estimates for the values of a and b. (This is equivalent to performing a weighted least-squares with weights $w = 1/C^2$; see reference (3), page 108 for details). Equation (2) can easily be converted to the desired relationship given by Equation (1). The intercept (b) from Equation (2) becomes the slope (b) for Equation (1) and slope (a) from Equation (2) becomes the intercept (a) for Equation (1). Equation (1) can be used to calculate the percent recovery over the applicable range of concentrations used in the study.

The percent recovery is given by

$$\text{Percent Recovery} = \left[\frac{a + b \cdot C}{C}\right] \times 100 = \left[\frac{a}{C} + b\right] \times 100 \qquad (3)$$

If the absolute value of the ratio (a/C) is small relative to the slope (b) for concentration in the low end of the range of concentration levels used in the study, then the percent recovery can be approximate by b x 100. For example, suppose the true concentration values range from 25 µg/L to 515 µg/L, the fitted line is given by $X = 0.20 + (0.85 \cdot C)$. The percent recovery would be approximated by (0.85) x 100 = 85 percent over the specified range of 25 µg/L to 515 µg/L.

If the absolute value of the ratio (a/C) is not small relative to the slope (b), then the percent recovery depends upon the true concentration (C), and it must be evaluated at each concentration value within the specified range.

## STATEMENT OF METHOD PRECISION

The precision of the method is characterized by the relationships between precision statistics (S and $S_r$) and mean recovery ($\bar{X}$). In order to obtain a mathematical expression for these relationships, regression lines of the form

$$S = d + e \cdot \bar{X} \qquad (4)$$

and

$$S_r = f + g \cdot \bar{X}^* \qquad (5)$$

were fitted to the data.

As discussed previously with respect to bias, the values of $\bar{X}$ and $\bar{X}^*$ often vary over a wide range. In such cases the standard deviation statistics associated with the larger mean recovery values will dominate the regression lines. This

will produce relatively larger errors in the estimates of S and $S_r$ at lower mean recovery values. Therefore, a weighted least squares technique was used to establish the values of the parameters d, e, f, and g in Equations (4) and (5). The weighted least squares technique was performed by dividing both sides of Equation (4) by $\bar{X}$ resulting in Equation (6).

$$\frac{S}{\bar{X}} = d \cdot \frac{1}{\bar{X}} + e \qquad (6)$$

and dividing both sides of Equation (5) by $\bar{X}^*$ resulting in Equation (7)

$$\frac{S_r}{\bar{X}^*} = f \cdot \frac{1}{\bar{X}^*} + g \qquad (7)$$

The $(S/\bar{X})$ values were regressed against the $(1/\bar{X})$ values and the $(S_r/\bar{X}^*)$ values were regressed against the $(1/\bar{X}^*)$ values using ordinary least squares to obtain estimates for the parameters d, e, f, and g.

Equations (4) and (5) were obtained from Equations (6) and (7) in a manner similar to that discussed for mean recovery. The slope (d) for Equation (6) is the intercept (d) for Equation (4), and the intercept (e) for Equation (6) is the slope (e) for Equation (4). Similarly, the slope (f) for Equation (7) is the intercept for Equation (5), and the intercept (g) for Equation (7) is the slope (g) for Equation (5).

Given Equations (4) and (5), the percent relative overall standard deviation and the percent relative single-analyst standard deviation are

$$\% \text{ RSD} = \left[\frac{d}{\bar{X}} + e\right] \times 100 \qquad (8)$$

and

$$\% \text{ RSD-SA} = \left[\frac{f}{\bar{X}} + g\right] \times 100 \qquad (9)$$

respectively. If absolute value of the ratio ($d/\bar{X}$) is small relative to the slope (e), then the percent relative overall standard deviation can be approximated by (e x 100) over the applicable range of mean recovery values. Similarly if the absolute value of the ratio ($f/\bar{X}^*$) is small relative to the slope (g), then the percent relative single-analyst standard deviation can be approximated by (g x 100) over the applicable range of mean recovery values.

If the ratios ($d/\bar{X}$) and ($f/\bar{X}^*$) are not small relative to the slopes (e) and (f), then the percent relative standard deviations depend upon the values of the mean recovery statistics $\bar{X}$ and $\bar{X}^*$, and they should be evaluated separately for each value of $\bar{X}$ and $\bar{X}^*$.

## COMPARISON OF BIAS AND PRECISION ACROSS WATER TYPES

It is possible that the bias and precision of the Interim Method 450.1 depend upon the water being analyzed. The summary statistics $\bar{X}$, S and $S_r$ are calculated separately for each concentration level within each water type. They can be compared across water types in order to obtain information about the effects of water type on bias and precision. However, the use of these summary statistics in this manner has several disadvantages. First, it is cumbersome since there are six mean recovery statistics ($\bar{X}$) (six concentrations) six precision statistics (S) and six precision statistics ($S_r$) calculated for each compound. Comparison of these statistics across concentration levels and across water types becomes unwieldly. Second, the statistical properties of this type of comparison procedure are difficult to determine.

An alternative approach, described in detail in Reference (6), has been developed to test for the effects of water type. This alternative approach is based on the concept of summarizing the average effect of water type across concentration levels rather than studying the local effects at each

concentration level. If significant differences are established by this alternative technique, then the summary statistics can be used for further local analysis.

The test for the effect of water type is based on the following statistical model. If $X_{ijk}$ denotes the measurement reported by laboratory i, for water type j, and concentration level k, then

$$X_{ijk} = \beta_j \cdot C_k^{\gamma_j} \cdot L_i \cdot \epsilon_{ijk} \qquad \begin{matrix} i = 1,2,\ldots, n \\ j = 1 \\ k = 1,2 \end{matrix} \tag{10}$$

The model components $\beta_j$ and $\gamma_j$ are fixed parameters which determine the effect of water type j on the behavior of the observed measurements ($X_{ijk}$). The parameter $C_k$ is the true value associated with concentration level k. The model component $L_i$ is a random factor which accounts for the systematic error associated with laboratory i. The model component $\epsilon_{ijk}$ is the random factor which accounts for the within-laboratory error.

The model is designed to approximate the global behavior of the data. The multiplicative structure was chosen because of two important properties. First, it allows for a possible curvilinear relationship between the data ($X_{ijk}$) and the true concentration level $C_k$ through the use of the exponent $\gamma_j$ on $C_k$. This makes the model more flexible in comparison to straight line models. Second, as will be seen below, there is an inherent increasing relationship between the variability in the data and the concentration level $C_k$ in this model. This property is important because it is typical of interlaboratory data collected under conditions where the true concentration levels vary widely.

Bias is related directly to the mean recovery or expected value of the measurements ($X_{ijk}$). The expected value for the data modeled by Equation (10) is

$$E(X_{ijk}) = n_j \cdot C_k^{\gamma_j} \cdot E(L_i \cdot \epsilon_{ijk}) \tag{11}$$

Precision is related to the variability in the measurements ($X_{ijk}$). The variance of the data modeled by Equation (10) is

$$\text{Var}(X_{ijk}) = \left[\beta_j C_k^{\gamma_j}\right]^2 \quad \text{Var}\,(L_i \cdot \varepsilon_{ijk}) \quad (12)$$

which is an increasing function of $C_k$.

The bias and precision of the method for TOX analysis depend upon water types through Equations (11) and (12) and the parameters ($\beta_j$) and ($\gamma_j$). If the ($\beta_j$) and ($\gamma_j$) vary with j (i.e., vary across water type), then the bias and precision of the method also vary across water type.

In order to determine if these parameters do vary across water type and to compare their values, they must be estimated from the laboratory data using regression techniques. Equation (10) represents the basic model. However, taking natural logarithms of both sides of Equation (10), the following straight line regression model is obtained

$$\ell n\, X_{ijk} = \ell n\, \beta_j + \gamma_j\, \ell n\, C_k + \ell n\, L_i + \ell n\, \varepsilon_{ijk} \quad (13)$$

which can be analyzed using standard linear model analysis techniques. The parameter $\ell n\ \beta_j$ is the intercept and $\gamma_j$ the slope of the regression line associated with water type j. It is assumed that $\ell n\ L_i$ is normally distributed with mean 0 and variance $\sigma_L^2$, and that $\ell n\ \varepsilon_{ijk}$ is normally distributed with mean 0 and variance $\sigma_\varepsilon^2$, and that the ($\ell n\ L_i$) and ($\ell n\ \varepsilon_{ijk}$) terms are independent.

Based on Equation (13) the comparison of water types reduces to the comparison of straight lines. The reagent water is viewed as a control, and the remaining lines (for surface or groundwater) are compared directly to the line for the reagent water.

Using the data on the log-log scale and regression techniques, the parameters $\ell n \beta_j$ (and hence $\beta_j$) and $\gamma_j$ can be estimated. The estimates are then used to test the null hypothesis that there is no effect due to water type. The formal null and alternative statistical hypotheses $H_0$ and $H_A$ are given by

$$H_0: \ell n \beta_j - \ell n \beta_1 = 0 \text{ and } \gamma_j - \gamma_1 = 0 \text{ for } j = 2,3$$

versus

$$H_A: \ell n \beta_j - \ell n \beta_1 = 0 \text{ and/or } \gamma_j - \gamma_1 = 0 \text{ for } j = 2,3$$

The test of null hypothesis is $H_0$ against the alternative hypothesis $H_A$ is based on F-statistic derived from standard linear model theory. The probability of obtaining a value of an F-statistic as large as the value which was actually observed, (F 0BS), denoted by P(F>F 0BS), is calculated under the assumption that $H_0$ is true. The null hypothesis $H_0$ is rejected in favor of $H_A$ if P(F>F 0BS) is less than 0.05.

If $H_0$ is rejected, then some linear combination of the differences $\ell n \beta_j - \ell n \beta_1$ and $\gamma_j - \gamma_1$ is statistically different from zero. However, this does not guarantee there will be a statistically significant direct effect attributable to any specific water type since the overall F test can be overly sensitive to minor systematic effects common to water types. The effect due to a specific water type is judged to be statistically significant only if one of the differences $(\ell n \beta_j - \ell n \beta_1)$ and/or $(\gamma_j - \gamma_1)$ is statistically different from zero. This is determined by checking the simultaneous 95 percent confidence intervals which are constructed for each of these differences. Each true difference can be stated to lie within its respective confidence interval with 95 percent confidence. If zero is contained within the confidence interval, then there is no evidence that the corresponding difference is signficantly different from zero.

If at least one of the confidence intervals for the differences ($\ell n\ \beta_j - \ell n\ \beta_1$) or ($\gamma_j - \gamma_1$) fails to include zero, then the statistical signifiance of the effect due to water type has been established. However, establishment of a statistically significant effect due to water type does not necessarily mean that the effect is of practical importance. Practical importance is related to the size and interpretation of the difference.

The interpretation of the differences involves comparing the mean recovery and standard deviation of the ($X_{ijk}$) data for each water type to the mean recovery and standard deviation obtained for reagent water. These comparisons are made on a relative basis. The mean recovery for water type j is given by Equation (11). The mean recovery for water type j is compared to that for reagent water (j=1) on a relative basis by

$$\frac{E(X_{ijk})}{E(X_{i1k})} = \frac{\beta_j\, C_k^{\gamma_j}\, E(L_i \cdot \varepsilon_{ijk})}{\beta_1\, C_k^{\gamma_1}\, E(L_i \cdot \varepsilon_{i1k})} = \frac{\beta_j}{\beta_1}\ C_k^{(\gamma_j - \gamma_1)} \qquad (14)$$

(The ratio of the standard deviations would be equivalent to Equation (14), and therefore the interpretation of the effect on precision is the same as that for the effect on mean recovery).

The ratio in Equation (14) is a measure of the relative difference in mean recovery between water type j and reagent water. It is comprised of two parts (a) $\beta_j/\beta_1$, which is independent of the true concentration level (i.e., the constant bias), and (b) $C_k^{(\gamma_j - \gamma_1)}$ which depends upon the true concentration level (i.e. the concentration dependent bias). If ($\gamma_j - \gamma_1$) is zero, then the relative difference in mean recovery is just $\beta_j/\beta_1$ which is independent of concentration level $C_k$. It can then be stated that the mean recovery from water type j is ($\beta_j/\beta_1$) x 100 percent of the mean recovery from the reagent water. If ($\gamma_j - \gamma_1$) is not zero, then the mean recovery from water type j is $((\beta_j/\beta_1)\ C_k^{(\gamma_j - \gamma_1)}$ x 100 percent of that from reagent water, and therefore depends upon the true concentration level $C_k$.

In order to illustrate these points, consider the following example which compares at least five water types. Suppose that a significant F-value has been obtained, and the confidence intervals for all the differences contain zero except for water type 5. For water type 5, the point estimate for $(\ell n\, \beta_5 - \ell n\, \beta_1)$ is -0.38 and the confidence interval for $(\ell n\, \beta_5 - \ell n\, \beta_1)$ is (-0.69, -0.07). The points estimate for $(\gamma_5 - \gamma_1)$ is 0.07, and the confidence interval for $(\gamma_5 - \gamma_1)$ is (-0.04, 0.18). In this case a statistically signficant effect due to water type has been established which involves only water type 5. The practical significance of this effect is judged by considering Equation (14). The ratio of mean recoveries from water type 5 and reagent water is given by

$$\frac{E(X_{i5k})}{E(X_{ilk})} = \frac{\beta_5}{\beta_1} C_k \quad (\gamma_5 - \gamma_1) \tag{15}$$

and the ratio of the standard deviations is given by

$$\sqrt{\frac{Var(X_{ijk})}{Var(X_{ilk})}} = \frac{\beta_5}{\beta_1} C_k \quad (\gamma_5 - \gamma_1) \tag{16}$$

Since the confidence interval for $(\gamma_5 - \gamma_1)$ contains zero this difference is assumed to be insignificant and is set to zero. Therefore Equations (15) and (16) reduce to $\beta_5/\beta_1$. The point estimate for $(\ell n \beta_5 - \ell n \beta_1)$ was -0.38.

Therefore, the point estimate for $\beta_5/\beta_1$ is 0.68, and the mean recovery from water type 5 is estimated to be 68 percent of the mean recovery from reagent water. Similarly the standard deviation for the data for water type 5 is estimated to be 68 percent of the standard deviation for the reagent water. Since the 95 percent confidence interval for $(\ell n \beta_5 - \ell n \beta_1)$ was (-0.69, -0.07), any value in the interval (0.50, 0.93) is a reasonable estimate for $\beta_5/\beta_1$, and the mean recovery (standard deviation) for water type 5 can be claimed to be from 50 percent to 93 percent of the mean recovery (standard deviation) for reagent water. The practical significance of the effect due to water type 5 would depend upon the importance of a mean recovery (standard deviation) observed for reagent water.

## SECTION 6

## RESULTS AND DISCUSSION

### OUTLIERS

Three levels of outlier testing were performed on the data collected in this study. The Cochran's test for homogeneity of variance was conducted in addition to the tests that are part of the IMVS package. By performing Cochran's test both before and after the standard IMVS package, it was determined that Cochran's testing prior to the IMVS run did not affect the results of the laboratory ranking or individual outlier tests. In the raw data Tables C-1 through C-4, data rejected by Cochran's test are indicated by "*CO" in the data columns. Data rejected as individual outliers are marked "*" in the data columns. Laboratory outliers are designated by an asterisk in the "lab rejected" column. The three tests used in this study rejected 28 of 220 data points, or 12.7 percent of the data.

### STATISTICAL SUMMARY

After outliers were rejected using the tests above, retained data were statistically analyzed. A summary of those analyses are presented in Table 6.

The statistical parameters included are:

a. n, Number of data points: the number of laboratories that submitted data which were not outliers.

b. T, True value, µg/L: theoretical TOX concentration of the sample based on weighed amounts of compounds added.

TABLE 6. STATISTICAL SUMMARY FOR TOX ANALYSES BY WATER TYPE

| | REAGENT WATER | | SURFACE WATER | | GROUND WATER | | CHLORINATED DRINKING WATER | |
|---|---|---|---|---|---|---|---|---|
| LOW YOUDEN PAIR | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| NUMBER OF DATA POINTS (n) | 9 | 10 | 9 | 8 | 8 | 9 | 8 | 10 |
| TRUE CONC (T) uG/L | 38.7 | 54.2 | 38.7 | 54.2 | 38.7 | 54.2 | – | – |
| MEAN RECOVERY (X) | 45.3 | 58.3 | 40.2 | 58.7 | 40.7 | 55.6 | 63.8 | 83.6 |
| BIAS (%REL ERROR) | 17.17 | 7.57 | 3.79 | 8.41 | 5.26 | 2.64 | – | – |
| OVERALL STD DEV (S) | 14.4 | 12.3 | 2.9 | 8.0 | 2.9 | 8.1 | 3.1 | 7.9 |
| OVERALL REL STD DEV, % | 31.85 | 21.18 | 7.24 | 13.56 | 7.18 | 14.61 | 4.9 | 9.5 |
| SINGLE STD DEV, (Sr) | 12.3 | | 6.7 | | 5.7 | | 4.5 | |
| ANALYST REL DEV, % | 23.67 | | 13.52 | | 11.80 | | 6.1 | |
| MEDIUM YOUDEN PAIR | 3 | 4 | 3 | 4 | 3 | 4 | 3 | 4 |
| NUMBER OF DATA POINTS (n) | 9 | 10 | 8 | 9 | 8 | 8 | 9 | 10 |
| TRUE CONC (T) uG/L | 193.4 | 243.7 | 193.4 | 243.7 | 193.4 | 243.7 | – | – |
| MEAN RECOVERY (X) | 161.6 | 211.9 | 178.8 | 229.8 | 178.9 | 223.2 | 137.8 | 178.5 |
| BIAS (%REL ERROR) | -16.45 | -13.04 | -7.57 | -5.70 | -7.48 | -8.42 | – | – |
| OVERALL STD DEV (S) | 7.1 | 14.1 | 5.7 | 12.8 | 8.8 | 8.1 | 12.7 | 29.6 |
| OVERALL REL STD DEV, % | 4.38 | 6.66 | 3.21 | 5.59 | 4.93 | 3.62 | 9.2 | 16.6 |
| SINGLE STD DEV, (Sr) | 9.3 | | 7.9 | | 4.5 | | 22.8 | |
| ANALYST REL DEV, % | 4.98 | | 3.87 | | 2.24 | | 14.4 | |
| HIGH YOUDEN PAIR | 5 | 6 | 5 | 6 | 5 | 6 | | |
| NUMBER OF DATA POINTS (n) | 10 | 8 | 7 | 8 | 9 | 8 | | |
| TRUE CONC (T) uG/L | 386.7 | 441.1 | 386.7 | 441.1 | 386.7 | 441.1 | | |
| MEAN RECOVERY (X) | 332.0 | 378.2 | 349.0 | 392.2 | 352.0 | 404.2 | | |
| BIAS (%REL ERROR) | -14.16 | -14.27 | -9.76 | -11.09 | -8.97 | -8.37 | | |
| OVERALL STD DEV (S) | 12.0 | 14.3 | 15.4 | 14.9 | 10.4 | 12.8 | | |
| OVERALL REL STD DEV, % | 3.61 | 3.79 | 4.41 | 3.81 | 2.96 | 3.16 | | |
| SINGLE STD DEV, (Sr) | 12.0 | | 10.9 | | 9.4 | | | |
| ANALYST REL DEV, % | 3.39 | | 2.93 | | 2.49 | | | |

c. $\bar{X}$, Mean recovery, µg/L: overall mean of the retained data.

d. Bias as percent relative error: difference between mean recovery and true value as a percentage of the true value.

e. S, Overall standard deviation, µg/L: standard deviation of $X_i$ values.

f. Overall relative standard deviation, percent: standard deviation of $X_i$ values as a percentage of $\bar{X}$ .

g. $S_r$, single-analyst standard deviation, µg/L: standard deviation for a given Youden pair (as described in the Statistical Treatment Section).

h. Single-analyst relative standard deviation, percentage: $S_r$ as a percentage of $\bar{X}$ .

## STATEMENTS OF BIAS AND PRECISION

The regression equations found in Table 7 indicate the performance that can be expected from routine use of Method 450.1. The bias of the method is estimated from the recovery regression equations in the first column of Table 7. In most studies of this kind, the slope of the equation is used to estimate the percent recovery for each concentration level and water type. The validity of using the slope to estimate recovery depends upon the magnitude of the intercept. If the intercept is considered negligible or at least insignificant, the slope may be considered a reliable estimator of recovery. If the intercept is large compared to the slope, the intercept itself contributes the most to estimates of recovery.

Examination of the statistical summary, Table 6, for reagent water indicates that the recovery for the low Youden pair was 107.5 to 117.2 percent, while

TABLE 7. REGRESSION EQUATIONS FOR PRECISION AND BIAS

| Water Type | $\bar{X}$ | S | $S_r$ |
|---|---|---|---|
| Reagent | $\bar{X} = 0.807C + 14.1$ | $S = -0.0128\ \bar{X} + 14.2$ | $S_r = -0.0092\ \bar{X} + 12.7$ |
| Surface | $\bar{X} = 0.894C + 7.14$ | $S = 0.0374\ \bar{X} + 2.68$ | $S_r = -0.0109\ \bar{X} + 6.14$ |
| Ground | $\bar{X} = 0.896C + 6.38$ | $S = 0.0280\ \bar{X} + 3.40$ | $S_r = 0.0033\ \bar{X} + 5.48$ |
| Chlorinated Drinking Water | — | $S = 0.0946\ \bar{X} - 9.22$ | $S_r = 0.1037\ \bar{X} - 0.1014$ |

$\bar{X}$ = Mean recovery (bias) as µg/L
S = Overall precision as µg/L
$S_r$ = Single-analyst precision as µg/L
C = True value as µg/L

those of the medium and high Youden pairs ranged from 83.5 to 92.4 percent. Inspection of the recovery regression equation for reagent water clearly indicates that the intercept is large compared to the slope because the actual recoveries obtained for all Youden pairs far exceed the 80.7 percent suggested by the slope of the regression equation.

In contrast, the slope of the recovery regressions for ground and surface waters predict recoveries of about 89 percent, while the recoveries actually observed for the medium and high Youden pairs ranged from 88.9 to 94.3 percent. The low Youden pairs for all water types gave actual recoveries in excess of 100 percent. The most probable causes for the positive bias at low concentrations are contamination of the columns during preparation and contamination of the analytical system in general when the samples are transferred from the adsorption column to the pyrolysis oven.

The algebraic relationship that guides the interpretation of the recovery regressions also applies to those for overall precision S and single-analyst precision $S_r$. These equations suggest that neither S nor $S_r$ depend significantly on concentration as evidenced by the unusual appearance of very small or negative slopes coupled with relatively large intercepts. The regressions for S for ground and surface waters, however, indicate slightly more dependence of S on concentration. The extraordinarily large intercepts associated with the S and $S_r$ regressions for distilled water are not easily explained. Examination of the raw data, (Appendix C), indicate that for all concentration levels the large values of S were not caused by erratic data from one or two laboratories. Moreover, the absolute S and $S_r$ values in the statistical summary, Table 6, for reagent water correspond closely to the intercepts of the regression for S and $S_r$, it is difficult to dismiss the equations as invalid. The comparative sizes and slopes and intercepts of the equations for all waters suggest that the most significant contributors to the overall precision of TOX analyses are related not to characteristics of the sample, but to aspects of the method, such as sample and column manipulation and variable contribution of blanks.

Performance of the TOX method with chlorinated drinking water is discussed separately here because of the nature of the sample itself and the slightly different treatment of the study data. First, because the samples of this water type were not spiked, but prepared by dilution of a previously chlorinated drinking water, no true concentrations are available with which to calculate a regression for mean recovery ($\bar{X}$) against true value (T). Secondly, two rather than three Youden pairs were prepared, approximating the low and middle concentrations of the reagent, ground and surface waters discussed above. Table 7 gives the regressions for S and $S_r$. The regression for overall S takes an unusual form with its strongly negative intercept of -9.22. Because the regression was calculated from only four data points rather than the traditional six, the contribution from the highest S value of 29.6 for sample four is magnified at the low concentrations.

Performance of the method for analyzing this water type is best discussed not in terms of the regression equations but in terms of the actual S, and $S_r$ values obtained in the study (Table 6). The individual S values ranged linearly from 3.1 to 29.6 over the range of concentrations tested. Single-analyst precision also appeared to be concentration dependent, ranging from 4.5 for the low Youden pair to 22.8 for the middle pair.

## EFFECT OF WATER TYPES

A summary of the statistical analyses to determine the effect of water type on precision and bias is presented in Appendix C, Table C-5. Using the multiplicative model described by Outler and McCreary (3), surface water and groundwater were compared to reagent water which is viewed as a control. Statistical significance was not demonstrated for either comparison using the F-test.

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# APPENDIX A

# INTERIM METHOD 450.1

EPA 600/4-81-056

United States
Environmental Protection
Agency

EPA

# Research and Development

Total Organic Halide
Method 450.1 - Interim

## Prepared for

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# TOTAL ORGANIC HALIDE

Method 450.1

Interim

U. S. Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Physical and Chemical Methods Branch
Cincinnati, Ohio 45268

November 1980

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Method 450.1

1. Scope and Application

1.1 This method is to be used for the determination of Total Organic Halides as $Cl^-$ by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/L. Organic halides as used in this method are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine containing species are not determined by this method.

1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed

to remove any trapped inorganic halides, and is then pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400$^{o}$C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply

should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

4. Safety

The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400°C before use, to minimize contamination.

5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000-ng $Cl^-$ equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

6. Reagents

6.1 Sodium sulfite - 0.1 M, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg $NO_3^-$/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg $Cl^-$) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng $Cl^-$) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 Trichlorophenol standard, instrument-calibration - First, nitrate wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg $Cl^-$/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 Reagent water - Reagent water is defined as a water in which an

interferent is not observed at the method detection limit of each parameter of interest.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 mL of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2 Nitrate-wash blanks (Method Blanks) - Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations.

7.2.1 The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to

minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at $4^{o}C$ without headspace.

8.3 Adjust pH of the sample to approximately 2 with concentrated $HNO_3$ just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L; 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L.

9.3 Wash the columns-in-series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

10. Pyrolysis Procedure

10.1 The contents of each column is pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a $CO_2$-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an $O_2$-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at 800°C for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the 200°C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

13.3 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

14. Calculations

OX as $Cl^-$ is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

$C_1$ = µg $Cl^-$ on the first column in series

$C_2$ = µg $Cl^-$ on the second column in series

$C_3$ = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in L

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

| Model Compound | Dose µg/L | Dose as µg/L Cl | Average % Recovery | Standard Deviation | No. of Replicates |
|---|---|---|---|---|---|
| $CHCl_3$ | 98 | 88 | 89 | 14 | 10 |
| $CHBrCl_2$ | 160 | 106 | 98 | 9 | 11 |
| $CHBr_2Cl$ | 155 | 79 | 86 | 11 | 13 |
| $CHBr_3$ | 160 | 67 | 111 | 8 | 11 |
| Pentachlorophenol | 120 | 80 | 93 | 9 | 7 |

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

| Sample | Avg. halide ug Cl/L | Standard Deviation | No. of Replicates |
|---|---|---|---|
| A | 71 | 4.3 | 8 |
| B | 94 | 7.0 | 6 |
| C | 191 | 6.1 | 4 |

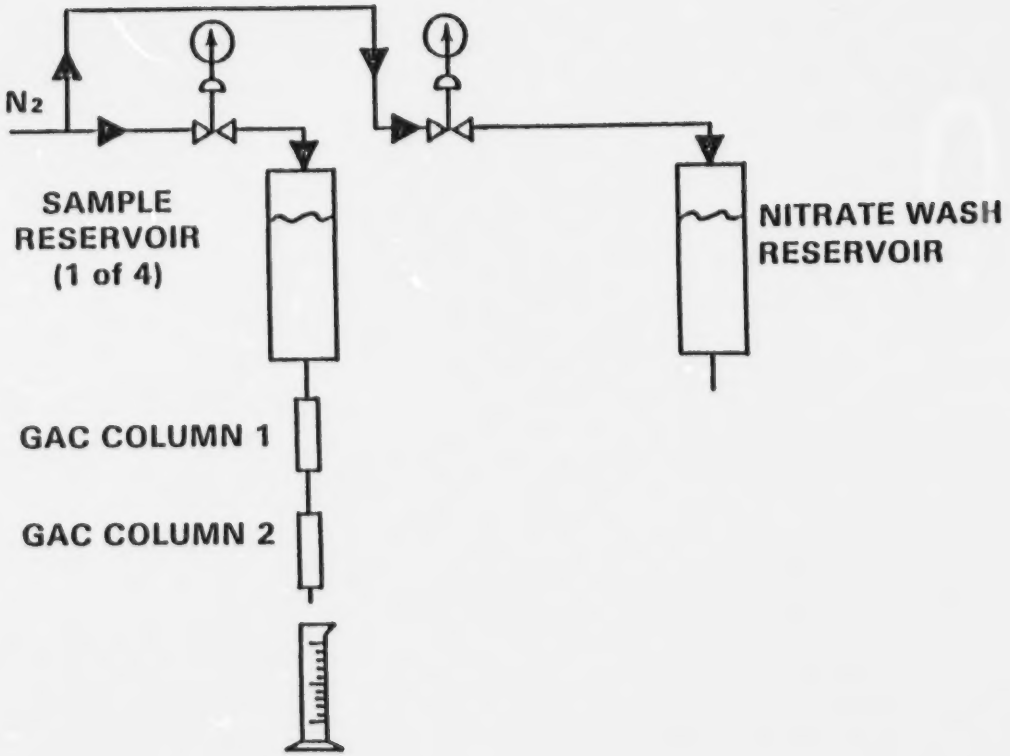


**Figure 1. Adsorption Schematic**

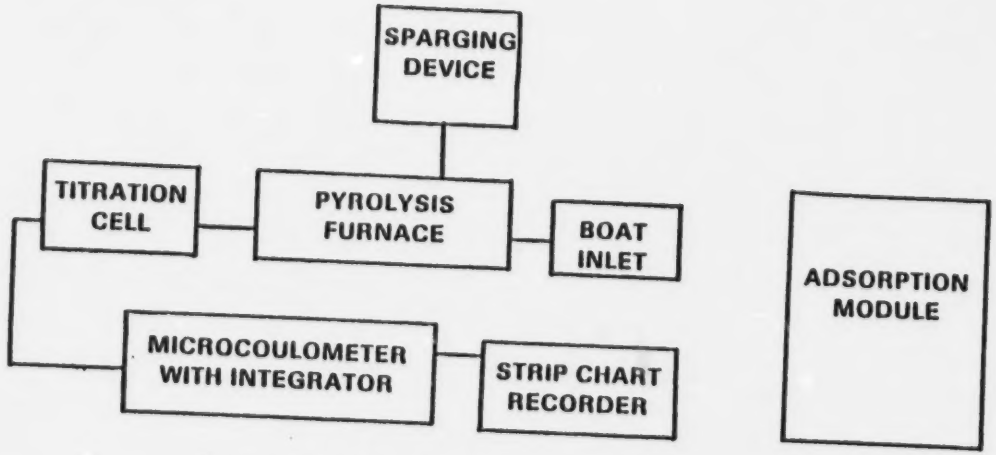


Figure 2. CAOX Analysis System Schematic

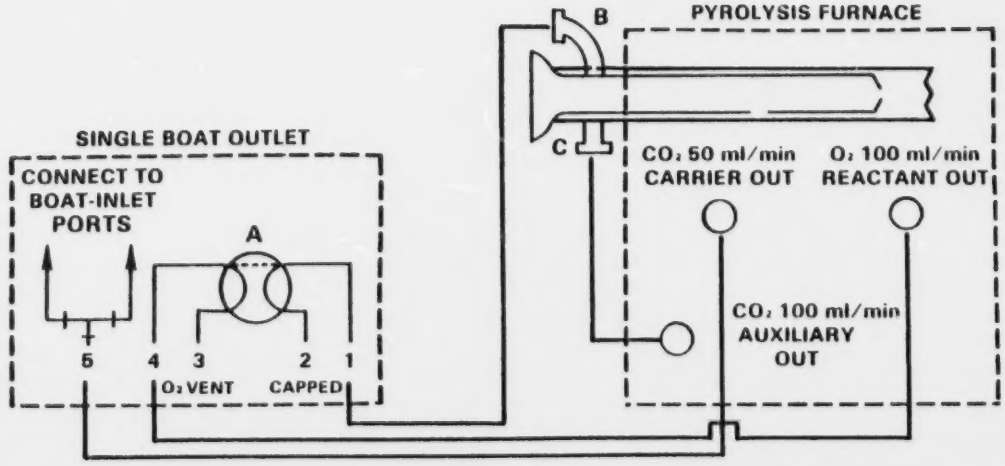


Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion, $O_2$ venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

## APPENDIX B

## INSTRUCTIONS TO PARTICIPATING LABORATORIES

January 7, 1985

Dear Participating Laboratory;

Please analyze the enclosed samples for Total Organic Halogen in strict accordance with United States Environmental Protection Agency Method 450.1 A copy of this method has been sent to your laboratory previously. Enclosed with this package is a note clarifying several points in the method. Each person receiving or relinquishing custody of the enclosed samples must complete the appropriate section of the enclosed sample custody record. Please include the date and time of arrival of this sample shipment on the custody record. Please store the samples in the dark and in a refrigerator until analysis.

Please retain the shipment container until after completion of the sample analysis. When analysis has been completed, return the sample bottle and blue ice packet to the container, seal the container, and address the container to our laboratory.

After we recieve your report of results for the sample analysis, we will contact United Parcel Service for round-trip shipment completion. UPS will pick up our shipment container and return it to our facility at no charge to you.

Also enclosed are two Statement of Conditions for Compliance forms. One form is to be signed by the chemist performing the TOX analysis. The other should be signed by the supervising chemist or laboratory director. These forms should be sent back to us along with the sample results.

A report of results, to the nearest 0.1 micrograms organic chloride per liter, should be sent to myself at Montgomery Laboratories.

THE REPORT OF RESULTS MUST BE RECEIVED BY DR. CLARK WITHIN FOURTEEN (14) DAYS OF SAMPLE RECEIPT.

Please enclose the two signed statement of condition forms; the chain of custody record; and all associated raw data information, including instrument readings, all blank, standard and sample measurements; any instrument malfunction or repair and loss of sample.

If you have any questions, please contact us.

Sincerely,

Robert R. Clark, PhD
Senior Chemist
Montgomery Laboratories
555 East Walnut
Pasadena, CA 91010
(818) 796-9141

**MONTGOMERY LABORATORIES**

a Division of James M. Montgomery, Consulting Engineers, Inc.
555 East Walnut Street, Pasadena, California 91101
(818) 796-9141/(213) 681-4255 Telex: 67-5420

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**CHAIN OF CUSTODY RECORD**

Client: Environmental Protection Agency

Contract Number: #68-03-3163

Preparer's Name: Eric Crofts

Sample Description: _____

Commments: _____

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**SAMPLE CUSTODY TRANSFER**

1. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

2. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

3. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

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**MONTGOMERY LABORATORIES**

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555 East Walnut Street, Pasadena, California 91101
(818) 796-9141/(213) 681-4255 Telex: 67-5420

## SAMPLE CUSTODY TRANSFER (Continued)

4. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

5. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

6. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

7. Relinquished By (Signature): _____

Date: _____ Time: _____

To: Organization's Name: _____
Received By (Signature): _____

Date: _____ Time: _____

Comments: _____

**STATEMENT OF CONDITIONS FOR COMPLIANCE WITH USEPA CONTRACT NO. 68-03-3163**

Laboratories subcontracting with J.M. Montgomery, Consulting Engineers, Inc. (JMM) to perform analyses for Total Organic Halogen (TOX) analyses in the evaluation of E.P.A. Interim Method 450.1, pursuant to United States Environmental Protection Agency (USEPA) Contract Number 68-03-3163, are required to comply with the following conditions:

1. The USEPA interim Method 450.1 must be strictly adhered to in the analysis of all samples provided pursuant to this contract. A copy of the method has previously been provided. Several clarifications to the method are enclosed.

2. The performance evaluation sample will be analyzed at no charge to JMM or the USEPA.

3. The individual chemist performing the analysis and the instrumentation used in the analysis of the performance evaluation sample will subsequently analyze all samples providied by JMM pursuant to this contract.

4. All raw data associated with the analysis of samples for this contract will be submitted to Dr. Robert R. Clark, 555 E. Walnut Street, Pasadena, CA, 91101. Raw data should include all blank, standard, and sample measurements; reports of any instrument malfunctions, maintenance and repair; and loss of sample.

5. A report of results to the nearest 0.1 microgram of organic chloride per liter, signed by the chemist performing the analyses and by the chemist's supervisor, will be submitted to Dr. Robert R. Clark within fourteen (14) days of sample receipt.

6. Complete written documentation of the raw data, quality control information, and maintenance records for the Xertex-Dohrmann Total Organic Halogen instrumentation shall be maintained throughout the time frame of this contract by the subcontracting laboratory, and will be submitted to JMM or the USEPA upon request.

7. A sample chain of custody form shall be signed and completed by each person taking or relinquishing custody of each sample, and upon completion of analysis the custody form will be submitted with the report of results to Dr. Clark.

I, _____ (Print Name) , _____ (Title)

for _____ (Company Name) on this day, _____ (Date) , 1984,

having read the above conditions, do agree to comply with these conditions in the analysis of all samples provided to me pursuant to U.S. Environmental Protection Agency Contract Number 68-03-3163.

_____
(Signature)

## CLARIFICATIONS TO METHOD

During phase 1 of this study, several questions arose concerning the wording of EPA Interim Methods 450.1. These notes are intended to clarify those points, to ensure that all participating laboratories use the same procedures.

### Section 7.2. Nitrate Wash Blanks (Method Blanks)

The method states that the repeatability of the method background must be established each day prior to sample analysis by analyzing "several" nitrate wash blanks. This has been further defined as at least three such blanks. Repeatability of later nitrate wash blanks is satisfactory if each measurement is within 20% of the mean of the previous blanks.

Spacing an additional nitrate wash blank between each group of eight pyrolyses is required so that the analyst can continually update the days' average nitrate wash value.

### Section 7.3. Blank Standards (Water Blanks)

The net results of the analyses of water blanks required in this section are intended as an indicator of the cleanliness of the system and to ensure lack of interferences. They are not used in any of the calculations for standards or samples.

### Section 7.2.1 and 9.3. Nitrate Washes on Single Columns

Some confusion was noted between these two sections of the method. Section 7.2.1 indicates that the nitrate wash blanks are obtained on single charcoal columns, washed as instructed for sample analysis section 9.3.

Please note that section 7.2.1 is referring not to column geometry in section 9.3 but to nitrate concentration and flow rate.

### Section 12. Breakthrough Calculations

This section states that "all second column measurements for a properly operating system not exceed 10% of the two column measurement." Note that the net second column measurement should not exceed 10% of the net two-column total measurement.

Since the sample size is only 250 mL and the analyst is required to perform two 100 mL filtrations, no sample would remain for analysis if breakthrough were indicated. Montgomery Laboratories can supply a limited number of replacement samples if problems are encountered.

## Section 14. Calculations using Nitrate Wash Blank (Method Blank)

Phase 1 results indicated that the average nitrate wash blank value was not being subtracted from adsorption efficiency standard values. It should also be subtracted from the blank standards (water blanks) to determine that the reagent water does not contain interferences or TOX concentrations that exceed the method detection limit. When calculations are required during the day to determine that analyses are within control limits, the average of the nitrate wash blanks obtained thus far for the day must be used in those calculations.

### Additional Instructions

1. The analyst must take precautions not to touch the charcoal or column plugs with the fingers. This can lead to serious contamination of the system. This problem can be avoided largely by using 1) the charcoal measuring scoop (available from Dohrman), and 2) a 2 mm ID stainless steel borer and ejection rod for cutting column plugs (also available from Dohrman). Clean hands (or even gloves) are essential when preparing the columns.

2. The sample reservoir should be rinsed with two 100 mL volumes of reagent water before adding another sample.

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## Water Analysis for TOTAL ORGANIC HALOGEN (TOX)

### Report of Instrument Data

Date: _____ Instrument Model No: _____

| Sample Description | Value Top Column Replicate 1 | Value Bottom Column Replicate 1 | Value Top Column Replicate 2 | Value Bottom Column Replicate 2 |
|---|---|---|---|---|
| Instrument Calibration Standard | _____ | *** | _____ | *** |
| Standard Blanks | _____ | _____ | _____ | _____ |
| Method Blanks | _____ | _____ | _____ | _____ |
| Method Blanks | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ |
| Instr. Calib. Std. or Method Blk* | _____ | *** | _____ | *** |
| _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ |
| Instr. Calib. Std. or Method Blk* | _____ | *** | _____ | *** |
| _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ |
| Instr. Calib. Std. or Method Blk* | _____ | *** | _____ | *** |
| _____ | _____ | _____ | _____ | _____ |
| _____ | _____ | _____ | _____ | _____ |
| Instr. Calib. Std. or Method Blk* | _____ | *** | _____ | *** |
| Adsorption Efficiency Standard | Amount spiked | | _____ | |
| | Value recovered | | _____ | |

* Circle one.
*** Second adsorption column in series not required.

Submitted By _____ Checked By _____

# APPENDIX C

# RAW DATA

TABLE C-1. RAW DATA FOR REAGENT WATER

| | | Low Youden Pair | | Medium Youden Pair | | High Youden Pair | |
|---|---|---|---|---|---|---|---|
| | | AMPUL 1 | AMPUL 2 | AMPUL 3 | AMPUL 4 | AMPUL 5 | AMPUL 6 |
| True Concentration in ug/L as Cl | | 38.7 | 54.2 | 193.4 | 243.7 | 386.7 | 441.1 |
| Laboratory | Lab Rejected | | | | | | |
| 1 | | 33.0 | 68.9 | 164.7 | 223.9 | 329.7 | 363.7 |
| 2 | | 38.2 | 51.5 | 158.1 | 199.7 | 319.9 | 386.5 |
| 3 | | 43.8 | 77.7 | 155.4 | 199.9 | 314.6 | 376.5 |
| 4 | | 64.4 | 70.5 | 164.9 | 203.7 | 336.2 | 376.1 |
| 5 | | 52.1 | 55.3 | 160.4 | 239.4 | 355.3 | 394.6*CO |
| 6 | | 70.9 | 50.7 | 159.8 | 196.4 | 337.6 | 360.2 |
| 7 | | 41.9 | 68.8 | 174.7 | 227.4 | 336.8 | 404.4 |
| 8 | | 28.4 | 38.8 | 150.1 | 207.3 | 336.3 | 370.7 |
| 9 | | 50.2*CO | 50.2 | 190.5* | 206.9 | 318.0 | 246.6*CO |
| 10 | | 35.3 | 50.3 | 166.1 | 214.7 | 335.1 | 387.3 |

* = Rejected, CO = Rejected by Cochran's Test

Current Significance Levels: 1. Lab Ranking Data Rejection Tests at 0.05 Significance Level
2. Individual Outlier Tests Using Thompson's Rule at 0.05 Significance Level

TABLE C-2. RAW DATA FOR SURFACE WATER

| | | Low Youden Pair | | Medium Youden Pair | | High Youden Pair | |
|---|---|---|---|---|---|---|---|
| | | AMPUL 1 | AMPUL 2 | AMPUL 3 | AMPUL 4 | AMPUL 5 | AMPUL 6 |
| True Concentration in ug/L in Cl | | 38.7 | 54.2 | 193.4 | 243.7 | 386.7 | 441.1 |
| Laboratory | Lab Rejected | | | | | | |
| 1 | | 39.0 | 52.6 | 177.1 | 209.8 | 327.3 | 399.5 |
| 2 | | 39.1 | 69.5 | 177.8 | 222.4 | 362.3 | 390.1 |
| 3 | | 35.1 | 58.9 | 167.4 | 218.7 | 327.5 | 375.0 |
| 4 | | 39.9 | 50.7 | 180.6 | 232.9 | 360.9 | 411.0 |
| 5 | | 44.2 | 97.2* | 184.7 | 253.1 | 361.3 | 389.1 |
| 6 | | 41.6 | 55.5 | 186.2 | 231.7 | 350.8 | 402.4 |
| 7 | | 42.6 | 56.1 | 179.2 | 243.0 | 217.3* | 456.4* |
| 8 | * | 31.6* | 46.4* | 136.6* | 200.3* | 346.0* | 373.3* |
| 9 | | 37.2 | 72.4 | 97.3*CO | 229.9 | 182.4*CO | 367.2 |
| 10 | | 42.7 | 54.1 | 177.0 | 226.7 | 352.7 | 403.1 |

* = Rejected, CO = Rejected by Cochran's Test

Current Significance Levels: 1. Lab Ranking Data Rejection Tests at 0.05 Significance Level
2. Individual Outlier Tests Using Thompson's Rule at 0.05 Significance Level

TABLE C-3. RAW DATA FOR GROUNDWATER

| | | Low Youden Pair | | Medium Youden Pair | | High Youden Pair | |
|---|---|---|---|---|---|---|---|
| | | AMPUL 1 | AMPUL 2 | AMPUL 3 | AMPUL 4 | AMPUL 5 | AMPUL 6 |
| True Concentration in ug/L as Cl | | 38.7 | 54.2 | 193.4 | 243.7 | 386.7 | 441.1 |
| Laboratory | Lab Rejected | | | | | | |
| 1 | | 42.3 | 52.5 | 182.7 | 214.3 | 363.0 | 405.3 |
| 2 | | 43.4 | 52.7 | 177.8 | 216.5 | 354.3 | 387.0 |
| 3 | | 41.7 | 47.4 | 168.8 | 211.1 | 343.7 | 388.2 |
| 4 | | 39.1 | 66.9 | 185.4 | 231.0 | 354.0 | 418.3 |
| 5 | | 55.5*CO | 48.4 | 135.7* | 230.8 | 371.7 | 419.1 |
| 6 | | 38.3 | 57.8 | 184.5 | 225.4 | 341.4 | 414.3 |
| 7 | | 43.9 | 70.2 | 179.5 | 230.7 | 353.0 | 396.0 |
| 8 | * | 39.7* | 40.3* | 189.2*CO | 202.9* | 332.7* | 383.5* |
| 9 | | 35.3 | 48.9 | 163.3 | 270.5* | 340.3 | 235.9*CO |
| 10 | | 41.8 | 55.6 | 189.4 | 225.7 | 346.7 | 405.1 |

* = Rejected, CO = Rejected by Cochran's Test

Current Significance Levels: 1. Lab Ranking Data Rejection Tests at 0.05 Significance Level
2. Individual Outlier Tests Using Thompson's Rule at 0.05 Significance Level

TABLE C-4. RAW DATA FOR CHLORINATED DRINKING WATER

| | | Low Youden Pair | | Medium Youden Pair | |
|---|---|---|---|---|---|
| | | AMPUL 1 | AMPUL 2 | AMPUL 3 | AMPUL 4 |
| Reference Value as ug/L as Cl | | 63.8 | 83.7 | 139.8 | 178.5 |
| Laboratory | Lab Rejected | | | | |
| 1 | | 60.9 | 81.0 | 123.8 | 147.6 |
| 2 | | 69.5 | 90.8 | 150.1 | 210.5 |
| 3 | | 60.7 | 77.1 | 134.2 | 147.0 |
| 4 | | 64.3 | 74.7 | 132.2 | 156.0 |
| 5 | | 64.0 | 78.0 | 148.7 | 176.2 |
| 6 | | 77.4*CO | 93.2 | 158.1*CO | 192.1 |
| 7 | | 66.3 | 97.9 | 161.2 | 172.5 |
| 8 | | 77.3* | 76.4 | 130.4 | 235.2 |
| 9 | | 60.6 | 83.7 | 124.5 | 195.2 |
| 10 | | 64.0 | 82.9 | 135.1 | 152.3 |

* = Rejected, CO = Rejected by Cochran's Test

Current Significance Levels: 1. Lab Ranking Data Rejection Tests at 0.05 Significance Level
2. Individual Outlier Tests Using Thompson's Rule at 0.05 Significance Level

TABLE C-5. EFFECT OF WATER TYPE ON TOX ANALYSIS

** POINT ESTIMATES **

REAGENT WATER SLOPE:GAMMA(1) = 0.88406

| WATER | INTERCEPT(WATER-REAGENT) | SLOPE(WATER-REAGENT) |
|---|---|---|
| 2 | -0.2035 | 0.0439 |
| 3 | -0.2587 | 0.0537 |

** ANALYSIS OF VARIANCE **

| SOURCE | DF | SUM OF SQUARES | MEAN SQUARE | F | PROB |
|---|---|---|---|---|---|
| REG(REAGENT) | 1 | 112.13997 | 112.13997 | | |
| REG(WATER/REAGENT) | 4 | 0.08406 | 0.02102 | 1.94 | 0.1071 |
| ERROR | 140 | 1.51648 | 0.01083 | | |
| TOTAL | 145 | 113.74052 | | | |

TABLE OF 95% CONFIDENCE INTERVALS FOR THE DIFFERENCES BETWEEN INTERCEPTS AND THE DIFFERENCES BETWEEN SLOPES

| WATER | INTERCEPT(WATER-REAGENT) ESTIMATE | INTERCEPT(WATER-REAGENT) INTERVAL | SLOPE(WATER-REAGENT) ESTIMATE | SLOPE(WATER-REAGENT) INTERVAL |
|---|---|---|---|---|
| 2 | -0.2035 | ( -0.4853 , 0.0783) | 0.0439 | ( -0.0109 , 0.0988) |
| 3 | -0.2587 | ( -0.5405 , 0.0231) | 0.0537 | ( -0.0010 , 0.1083) |

NOTE:
IF ZERO IS CONTAINED WITHIN A GIVEN CONFIDENCE INTERVAL THEN THERE IS NO STATISTICAL SIGNIFICANCE BETWEEN REAGENT WATER AND THE CORRESPONDING WATER FOR THE ASSOCIATED PARAMETER(INTERCEPT/SLOPE).

THE SLOPE AND INTERCEPT ESTIMATES FROM THIS ANALYSIS ARE NOT THE SAME AS THOSE OBTAINED FROM THE PRECISION AND ACCURACY REGRESSIONS PERFORMED EARLIER.